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Published in:
Chemical Engineering Science

DOI:
[10.1016/j.ces.2007.06.018](https://doi.org/10.1016/j.ces.2007.06.018)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

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Citation for published version (APA):

Haubrock, J., Hogendoorn, J. A., & Versteeg, G. F. (2007). The applicability of activities in kinetic expressions: A more fundamental approach to represent the kinetics of the system $\text{CO}_2\text{-OH--salt}$ in terms of activities. *Chemical Engineering Science*, 62(21), 5753-5769. <https://doi.org/10.1016/j.ces.2007.06.018>

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The applicability of activities in kinetic expressions: A more fundamental approach to represent the kinetics of the system $\text{CO}_2\text{--OH}^-$ –salt in terms of activities

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Received 22 October 2006; received in revised form 29 March 2007; accepted 11 June 2007

Available online 19 June 2007

Abstract

The applicability of utilizing activities instead of concentrations in kinetic expressions has been investigated using the reaction of CO_2 in sodium hydroxide solutions also containing different neutral salts (LiCl, KCl and NaCl) as model system. For hydroxide systems it is known that when the reaction rate constant is based on the use of concentrations in the kinetic expression, this “constant” depends both on the counter-ion in the solution and the ionic strength which is probably caused by the strong non-ideal behavior of various components in the solution. In this study absorption rate experiments have been carried out in the pseudo-first-order absorption rate regime. The experiments have been interpreted using a new activity based kinetic rate expression instead of the traditional concentration-based rate expression.

A series of CO_2 absorption experiments in different NaOH (1, 1.5, 2.0 mol l^{−1})–salt (LiCl, NaCl or KCl)–water mixtures has been carried out, using salt concentrations of 0.5 and 1.5 mol l^{−1} all at a temperature of 298 K. Interpretation of the data additionally required the use of an appropriate equilibrium model (needed for the calculation of the activity coefficients), for which, in this case, the Pitzer model was used. The additions of the salts proved to have a major effect on the observed absorption rate. The experiments were evaluated with the traditional concentration based-approach and the “new” approach utilizing activity coefficients. With the traditional approach, there is a significant influence of the counter-ion and the hydroxide concentration on the reaction rate. The evaluation of the experiments with the “new” approach—i.e. incorporating activity coefficients in the reaction rate expressions—reduced the influence of the counter-ion and the hydroxide concentration on the reaction rate constant considerably. The absolute value of the activity based-reaction rate constant $k_{\text{OH}^-}^m$ (γ) for sodium hydroxide solutions containing either LiCl, KCl or NaCl is in the range between 10 000 and 15 000 kg (kmol^{−1} s^{−1}) compared to the traditional approach where the value of the lumped reaction rate constant k_{OH^-} is between 7000 and 34 000 m³ (kmol^{−1} s^{−1}).

Therefore, it can be concluded that the application of the new methodology is thought to be very beneficial especially in processes where “the thermodynamics meet the kinetics”. Based on this it is anticipated that the new kinetic approach will first find its major application in the modeling of integrated processes like Reactive Distillation, Reactive Absorption and Reactive Extraction processes where both, thermodynamics and kinetics, are of essential importance and, additionally, activity coefficients deviate substantially from unity.

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Keywords: Absorption; Kinetics; Mass transfer; Mathematical modeling; Activity coefficients; Carbon dioxide

1. Introduction

The kinetics of CO_2 in caustic solutions, especially in sodium hydroxide solutions, have been extensively studied within the last decades by doing absorption rate experiments. In these studies it has been found that the reaction rate constant is not only dependent on the concentrations of the reacting species, but also affected by the ionic strength of the caustic solution

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$$\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}. \quad (2)$$

In the present study it is attempted to derive a generally applicable rate expression for the reaction of CO_2 with OH^- in mixed electrolyte solutions based on the activities of the species, and not on the commonly used concentrations. It is studied whether the new approach will yield a reaction rate constant that is (nearly) independent on the ionic strength and on the counter-cation in the solution, respectively.

New data obtained from CO₂ absorption experiments in sodium hydroxide solutions containing variable amounts of various dissociating salts (LiCl, NaCl or KCl) are presented and will be used to study the activity-based kinetic concept over a wide range of liquid compositions. For the activity-based approach it is of course necessary to use activity coefficients, and in this study the Pitzer model (Pitzer, 1973) has been used for this purpose. The newly developed kinetic expression is compared to the traditional approach where “only” concentrations are used.

2.1. Experimental setup and procedure

The absorption rate experiments needed to derive the kinetics of the reaction of CO_2 with OH^- were carried out in a stirred vessel with a smooth gas–liquid interface. The reactor was operated batchwise with respect to the gas and liquid phases (see Fig. 1). A similar setup was used by Derks et al. (2006) for measuring fast reaction kinetics hence the setup is only shortly described here. The reactor was completely made of glass, thermostated and consisted of an upper and lower part, sealed gas tight using an O-ring and screwed flanges. The reactor was equipped with magnetic stirrers in the gas (upper) and in the liquid phase (lower). The stirring speed could be controlled independently of one another. The dynamic pressure in the gas supply vessel was measured using a digital pressure transducer (Druck) while a constant pressure in the reactor was maintained

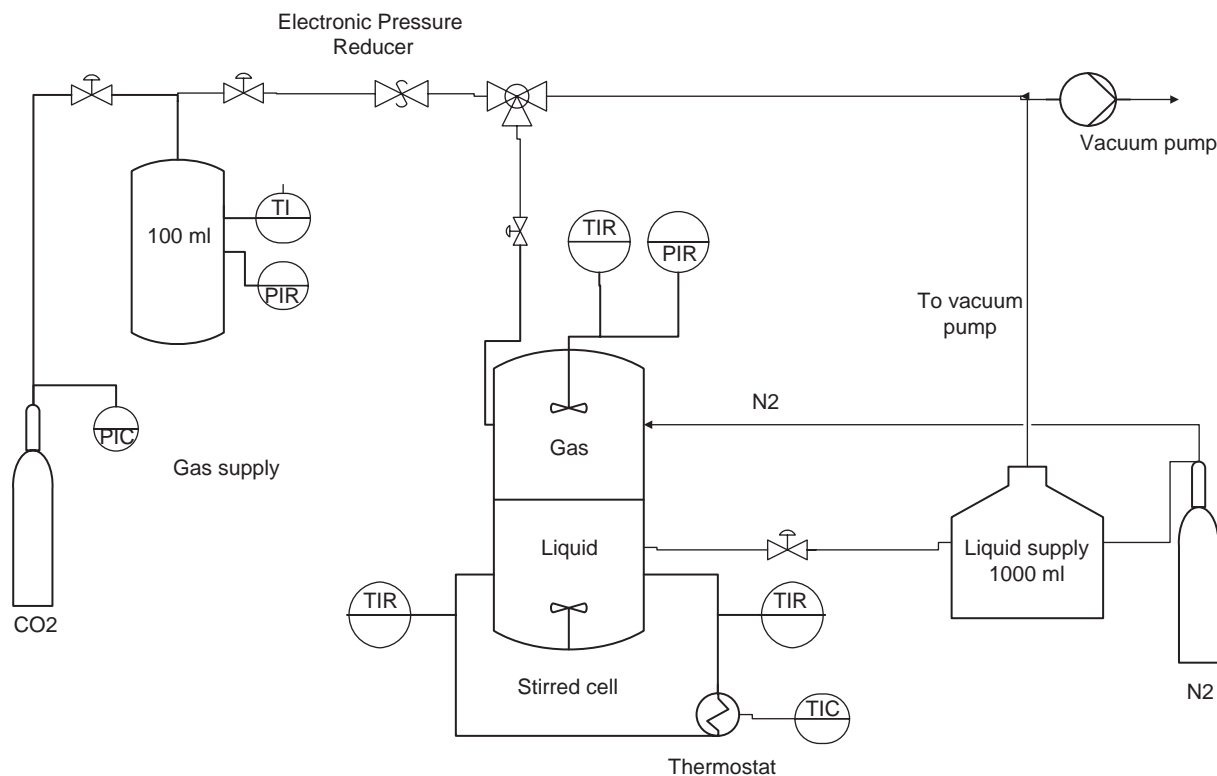


Fig. 1. Setup.

by using a pressure controller (Brooks 5866). The pressure in the reactor was monitored by a pressure transducer (Dresser), with a maximum absolute deviation of 0.15 mbar under the experimental conditions applied. Furthermore, the temperatures in the reactor and the gas supply vessel were measured by means of PT 100 elements. Pressures and temperatures were digitally recorded every second. The typical temperatures in the reactor and the CO₂ gas supply vessel were around 298 K and measured exactly during each experiment.

The partial CO₂ pressure in the reactor was set at a pressure between 6 and 16 mbar. The total volume of the reactor was 1070 ml whereof around 600 ml was filled with hydroxide solution. The horizontal gas–liquid contact area in the reactor was determined to be 71.5 cm². The gas supply vessel had a volume of 100 ml and the pressure in that vessel at the start of an experiment was close to 5 bar. The experimental procedure for a batch experiment was as follows: a freshly prepared alkaline-salt solution was charged into an evacuated reactor from the liquid supply vessel where it was shortly degassed under vacuum to remove possibly dissolved ambient gas. After that, the vapor–liquid equilibrium was allowed to establish in the reactor and the vapor phase pressure (p_{vap}) was noted. Pure CO₂ from the gas supply vessel was introduced into the reactor at a desired set-pressure which was maintained by the pressure controller. The CO₂ pressure was chosen to meet the conditions for absorption in the so-called pseudo-first-reaction regime (Danckwerts, 1970) under the respective experimental conditions. The stirrer in both phases was turned on and the pressure in the gas supply vessel was monitored for around 300 s. The pressure decrease in time is due to the absorption of CO₂ in the liquid and can be related to the kinetics if the experiments are carried out in the pseudo-first-order absorption regime.

Some experiments have been carried out to measure the physical solubility of N₂O. The physical solubility of N₂O is related to the physical CO₂ solubility via the well-known N₂O/CO₂ analogy (Laddha et al., 1981). For these measurements the procedure was slightly different than described above (see also Versteeg and Vanswaaij, 1988). In this case, after admittance of N₂O to the reactor, the valve between the supply vessel and the reactor was directly closed and thereafter equilibrium was awaited. The difference between the initial and end pressure of N₂O in the reactor can be used to determine the physical solubility of N₂O in the solution, and, therewith, the physical solubility of CO₂ in the same solution can be estimated. The experimental procedure was validated with solubility experiments of N₂O in water, for which extensive and reliable literature data are available (Versteeg and Vanswaaij, 1988; Xu et al., 1991). The physical solubility of N₂O as obtained for these validation experiments was within 5% of literature data.

3. Chemicals

Carbon dioxide (> 99.99 vol%; Hoekloos) was used without further purification. Sodium hydroxide (> 99% mass), sodium chloride (> 99.5% mass), lithium chloride (> 99% mass) and potassium chloride (> 99.5% mass) were purchased from

Merck and used as received. The solutions were prepared using deionized water and the actual hydroxide concentration was determined by potentiometric titration.

4. Determination of the reaction rate constant from experimental data

For fast gas–liquid reactions, a reliable determination of the forward reaction rate constant using an analytical evaluation method is only possible for irreversible pseudo-first-order reaction conditions as only in that regime an accurate analytical expression for the enhancement factor can be found (van Swaaij and Versteeg, 1992). Moreover, in the pseudo-first-order regime the mass transfer coefficient is not required for the evaluation of the experiments. Hence, a possible error introduced by the application of the mass transfer coefficient can be avoided. For irreversible reactions, reactions in the pseudo-first-order regime have to fulfill the subsequent two conditions:

$$Ha > 3, \quad (3)$$

$$\frac{E_{\infty}}{Ha} > 5. \quad (4)$$

The Hatta-number for a pseudo-first-order reaction is defined by Hikita and Asai (1976):

$$Ha = \frac{\sqrt{k_1 \cdot D_{\text{CO}_2\text{-solution}}}}{k_L} \quad (5)$$

with k_L being the mass transfer coefficient and k_1 being the pseudo-first-order reaction rate constant which traditionally reads as follows:

$$k_1 = k_{\text{OH}^-} \cdot c_{\text{OH}^-}. \quad (6)$$

The enhancement factor for instantaneous, irreversible reactions in terms of the film theory is expressed as follows (Baerns et al., 1992):

$$E_{\infty} = 1 + \frac{D_{\text{OH}^-\text{-solution}} c_{\text{OH}^-}}{D_{\text{CO}_2\text{-solution}} c_{\text{CO}_2}^{\text{interface}}}. \quad (7)$$

If the experimental conditions are chosen to obey the two relations 3 and 4, an approximate—but very accurate—analytical solution can be applied to interpret the experiments. The two above noted criteria (Eqs. 3 and 4) have been checked after every experiment to ascertain the condition of a pseudo-first-order reaction: in all experiments referred to in this paper the conditions of an irreversible pseudo-first-order reaction have been met. If the conditions for a pseudo-first-order reaction are fulfilled, the generic CO₂ absorption rate ($J_{\text{CO}_2} A$) is given by e.g. Kumar et al. (2003):

$$J_{\text{CO}_2} A = \sqrt{k_1 D_{\text{CO}_2\text{-solution}}} m_{\text{CO}_2, \text{solution}} p_{\text{CO}_2, t} \left(\frac{A}{RT} \right). \quad (8)$$

In this expression the implicit assumption of the CO₂ concentration in the liquid bulk being zero is included. During the

experiments the total pressure in the reactor was kept constant by the pressure controller. Hence the total pressure was in fact not depending on time. The partial pressure of CO₂ in the reactor was calculated from the experimentally observed pressure according to the following relation:

$$p_{\text{CO}_2, t=\text{const.}} = p_{\text{tot}, t=\text{const.}} - p_{\text{vap.}} \quad (9)$$

The absorption rate can then be calculated from the dynamic pressure in the gas supply vessel:

$$J_{\text{CO}_2} A = \frac{d p_{\text{Reservoir}, t}}{dt} \cdot \frac{V_{\text{Reservoir}, t}}{RT_{\text{Reservoir}, t}} \quad (10)$$

5. Physical properties employed in the interpretation of the flux data

For the evaluation of the experimental data reliable physical data are needed. Both the diffusion coefficient of CO₂ in the hydroxide–salt solutions as well as the physical solubility of CO₂ in these solutions are physical properties required for the evaluation of the experimental data. The dimensionless physical solubility of CO₂ in the hydroxide–salt solution has been estimated with the model suggested by Schumpe (1993). In this model the dimensionless solubility of CO₂ in mixed electrolyte solutions is given as

$$m_{\text{CO}_2, \text{solution}} = m_{\text{CO}_2, \text{water}} \left(\frac{c_{g,0}}{c_g} \right)^{-1} \quad (11)$$

where the ratio $c_{g,0}/c_g$ is defined as

$$\log \left(\frac{c_{g,0}}{c_g} \right) = \sum_i (h_i + h_g) c_i \quad (12)$$

The parameters h_i and h_g for the species of interest are given in Table 1 (Schumpe, 1993). To validate Schumpe's method for the estimation of the physical solubility of CO₂ in reactive solutions (as described by Eqs. (11) and (12)), a limited number of experimental determinations of the physical solubility of N₂O in hydroxide–salt solutions containing 1.5 kmol m^{−3} of the particular salt has been carried out according to the method as described in Section 2.

The experimental N₂O solubility was converted to the CO₂ solubility by using the well known CO₂/N₂O analogy (Laddha et al., 1981) to be able to compare the experimentally determined solubility to the CO₂ solubility predicted by Schumpe's method.

The values reported in Table 2 are dimensionless physical solubilities ($m_{\text{CO}_2-\text{Solution}}$) but can also be converted to the frequently encountered Henry coefficient using the following equation:

$$m_{i,j} = \frac{He}{RT} = \frac{(p^{\text{Initial}} - p^{\text{EQ}})}{p^{\text{EQ}}} \frac{V_{\text{gas}}}{V_{\text{liquid}}} \quad (13)$$

The experimentally derived dimensionless physical solubilities reported in Table 2 are approximately 20% lower compared

Table 1

Parameters needed for the determination of the dimensionless CO₂ solubility (Schumpe, 1993)

Cation	$h_i \text{ m}^3$ (kmol ^{−1})	Anion	$h_i \text{ m}^3$ (kmol ^{−1})	Gas	$h_i \text{ m}^3$ (kmol ^{−1})
Li	0.0691	OH [−]	0.0756	CO ₂	−0.0183
Na	0.1171	Cl [−]	0.0334		
K	0.0959				

Table 2

Dimensionless physical solubility $m_{\text{CO}_2-\text{Solution}}$ of CO₂ in caustic salt solutions derived from (1) Schumpe's method and (2) N₂O solubility experiments

c_{NaOH} (kmol m ^{−3})	Salt	c_{Salt} (kmol m ^{−3})	$m_{\text{CO}_2-\text{Solution}} [-]$	
			Schumpe	Own measurements
1.7558	LiCl	1.47	0.31	0.26
0.986	LiCl	1.5	0.42	0.36
1.9181	NaCl	1.5	0.24	0.21
0.9876	NaCl	1.5	0.35	0.32
1.9382	KCl	1.5	0.26	0.22
0.979	KCl	1.5	0.38	0.32

to those estimated with Schumpe's method (Schumpe, 1993). Assuming the CO₂/N₂O analogy also holds for these solutions, this indicates that the physical solubility of CO₂ in caustic salt solutions seems to be overpredicted with Schumpe's method with about 20% for all experiments. Nevertheless the estimation method exhibits the same trend as the (indirectly) measured CO₂ solubility and also predicts a substantially higher CO₂ solubility of solutions containing LiCl.

As experimental N₂O data were not determined for all combinations/concentrations of salts mixtures, no attempt has been made to adapt Schumpe's parameters and it was decided to utilize the physical solubilities estimated by Schumpe's method to evaluate the experimental absorption rate experiments to maintain consistency throughout this study.

The diffusivity of CO₂ in aqueous electrolyte solutions as needed in Eq. (8) was calculated from the application of the Stokes–Einstein relationship (Eq. (14)) and the diffusivity of carbon dioxide in water as given by Danckwerts (1970). The use of the Stokes–Einstein relationship is generally accepted in this form to calculate the diffusion coefficient of carbon dioxide in hydroxide solutions (Nijsing et al., 1959; Kucka et al., 2002).

$$D_{\text{Solution}} \mu_{\text{Solution}} = D_{\text{water}} \mu_{\text{water}} = \text{const.}, \quad (14)$$

$$\log D_{\text{CO}_2-\text{water}} = -8.176 + \frac{712.5}{T[\text{K}]} - \frac{2.591 * 10^5}{T[\text{K}]^2} \quad (15)$$

The viscosities of hydroxide–salt solutions containing 1.5 kmol m^{−3} and 0.5 kmol m^{−3} of the particular salt have been experimentally determined. The kinematic viscosities have been measured with a Lauda Processor Viscosity System 2.49e. This semi-automated system comprises an oil thermostat bath—in which the standardized capillary is immersed—and

Table 3
Viscosities of salt solutions at 25 °C

c_{NaOH} (kmol m ⁻³)	Salt	c_{Salt} (kmol m ⁻³)	ν (mm ² s ⁻¹)
0	LiCl	0.5	0.9811
1.006	LiCl	0.5	1.1415
1.983	LiCl	0.5	1.3810
0	LiCl	1.5	1.0981
0.986	LiCl	1.5	1.3149
1.7558	LiCl	1.5	1.5465
0	NaCl	0.5	0.9498
0.9010	NaCl	0.5	1.1041
1.9468	NaCl	0.5	1.3434
0	NaCl	1.5	0.9948
0.9876	NaCl	1.5	1.2297
1.9181	NaCl	1.5	1.5255
0	KCl	0.5	0.9045
1.0014	KCl	0.5	1.0610
1.9592	KCl	0.5	1.2792
0	KCl	1.5	0.8531
0.9790	KCl	1.5	1.0497
1.9382	KCl	1.5	1.2934

a control unit. The temperature of the oil bath could be controlled within ± 0.1 °C. The control unit is linked to a computer to program the control unit and to read out and store the residence times of the fluids in the capillary. The viscosity of every solution listed below has been measured five times. The deviation of the residence time was in all cases less than 3 s. This corresponds to an error of around 2–3% in the derived value of the diffusion coefficient. The measured kinematic viscosities are listed in Table 3.

For deriving the dynamic viscosities from the experimentally determined kinematic viscosities the following basic equation was applied (Bird et al., 1960):

$$\nu \cdot \rho = \mu. \quad (16)$$

As there are no data available on the density for the mixtures used in the experiments presented here, an estimation method had to be used. According to Sipos et al. (2001) the density of a pure NaOH/water mixture at 25 °C can be calculated with the following relation:

$$\rho = \rho_{\text{H}_2\text{O}} + 46.92210m_{\text{OH}^-} - 4.46892m_{\text{OH}^-}^{1.5} \quad (\text{g cm}^{-3}). \quad (17)$$

In this work it has been assumed that by replacing the molality m_{OH^-} in Eq. (17) by the total anion molality of the solution, the density of a mixed NaOH/salt/water mixture can be estimated. Although this seems like a rough approach, the following will show that it yields very acceptable results for the solutions of importance in this study.

First experimental liquid density data of the pure salt/water solutions (NaCl, KCl, LiCl and NaOH) (Lide, 2004) at 20 °C were compared at a concentration of 3.5 mol l⁻¹ (highest total concentration used in this study), as the difference in density is expected to increase with concentration. The experimental liquid density data from Lide (2004) have been used for interpolation to compare the liquid densities at exactly 3.5 mol l⁻¹.

The LiCl solution has a density of 1.079 g cm⁻³, the KCl solution a density of 1.153 g cm⁻³ and the NaCl solution a density of 1.133 g cm⁻³ whereas a 3.5 mol l⁻¹ NaOH solution has a liquid density of 1.135 g cm⁻³.

From the values given in the previous paragraph it can be concluded that all density values are within 6.5% of each other. Secondly, considering now that a 3.5 mol l⁻¹ salt solution as used in this study always contains 2 mol l⁻¹ NaOH and 1.5 mol l⁻¹ of LiCl, NaCl or KCl respectively, the density difference among these three 3.5 mol l⁻¹ solutions is most likely lower than 6.5%. The density difference of a pure salt/water solution (LiCl, NaCl and KCl, respectively) at 2 and 3.5 mol l⁻¹ has been calculated based on the experimental data of Lide (2004) and simply added to the liquid density of a 2 mol l⁻¹ NaOH solution to obtain an estimated density (assuming ideal mixing) for the mixture.

When comparing these “estimated” NaOH/salt/water densities with the liquid density of a single 3.5 mol l⁻¹ NaOH solution as predicted by Eq. (17), the relative differences were as follows: LiCl containing solution difference < 2.0%, NaCl containing solution difference < 0.2% and KCl containing solution difference < 0.9%.

These differences are so small, that it seems justified to estimate the densities of the solutions using the total anion molality in Eq. (17). The deviation of the k_{OH^-} values for LiCl-doped solutions due to uncertainty in the density (which affects the estimate of the viscosity and therewith the estimated diffusion coefficient) is estimated to be less than 2%. For NaCl-doped solutions this deviation is less than 0.5% and for KCl-doped solutions less than 1%.

It must be noted that some input parameters, like the physical solubility of CO₂ in the corresponding salt solution and the viscosity of the salt solution (which affects the value of the estimated corresponding diffusion coefficient, see Eq. (14)), have a strong influence on the derived reaction rate constant as determined using Eq. (8).

In this study, the required physical properties needed in the interpretation of the experiments (e.g. physical solubility of CO₂, diffusion coefficient of CO₂ in the solution) have always been evaluated at the actual composition of the solvent used and the actual reaction temperature of 25 °C. Considering the uncertainty in the aforementioned physical parameters and the experimental error in the current experiments, the overall uncertainty in the reaction rate constant is estimated to be 10%.

6. Experimental results and their interpretation using the traditional approach

For validation purposes absorption rate experiments of CO₂ in “pure” sodium hydroxide/water solutions have been carried out in the setup as described in Section 2, as for this solution many literature data on the kinetics are available. The experimental results of these validation experiments have been evaluated according to the method described in Section 4 of this study. The kinetic constants, as derived from the validation experiments carried out at different OH⁻ concentrations have been fitted to an OH⁻ concentration dependent equation

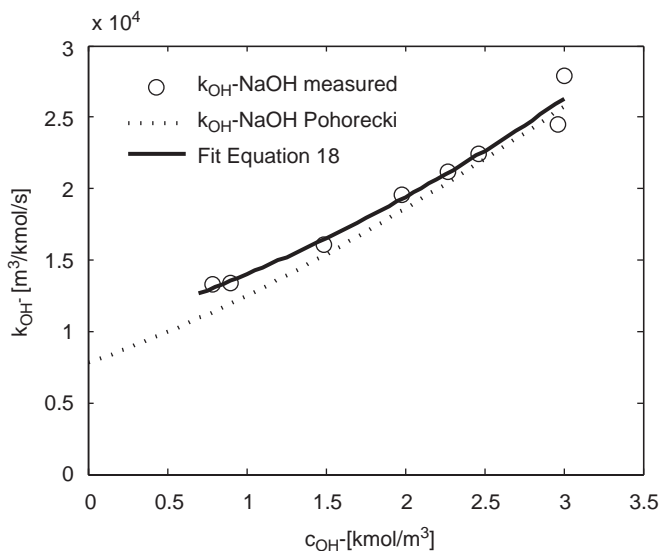


Fig. 2. Comparison between own measurements and results as predicted by Pohorecki for aqueous NaOH solutions.

having the form:

$$k_{\text{OH}^-}(T, I) = k_{\text{OH}^-}^{\text{inf}}(T = 25^\circ\text{C}) \cdot 10^{P_1 \cdot c_{\text{OH}^-}^2 + P_2 \cdot c_{\text{OH}^-}} \quad (18)$$

This equation has also been used by Pohorecki and Moniuk (1988). The applied fit criterion was the minimization of the squared errors between the measured k_{OH^-} values and the corresponding fitted values which yielded $k_{\text{OH}^-}^{\text{inf}} = 9904 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$, $P_1 = -4.51 \cdot 10^{-3} \text{ kmol}^2 \text{ m}^{-6}$ and $P_2 = 0.155 \text{ kmol m}^{-3}$. The resulting fit and the experimental data points are depicted in Fig. 2.

The maximum relative deviation between the rate constant derived from the present measurements and those of Pohorecki and Moniuk (1988) amounts to 14%, obtained for a hydroxide concentration of 0.8 kmol m^{-3} . For all other concentrations the difference between the prediction based on the experiments from this work and the prediction by the relation of Pohorecki was less than 10%. It can be concluded that the presently used experimental setup and procedure yields results that agree well with the results obtained with the correlation proposed by Pohorecki.

Moreover, the results also again clearly demonstrate that no real “constant” rate constant is encountered. To elucidate the influence of different cations on the reaction rate, experiments were carried out with NaOH-solutions to which LiCl, NaCl and KCl were added, respectively.

To study the influence of the type of cation on the reaction rate of CO_2 in a caustic solution, various solutions have been prepared and used. Table 4 below gives the matrix of all solutions employed in this study.

The results for the absorption of CO_2 in a sodium hydroxide solution with a varying amount of LiCl are presented in Fig. 3. Note that in Fig. 3 the kinetic constant is still expressed

Table 4

Matrix of solutions employed in the experimental study

c_{NaOH} (kmol m^{-3})	Salt	c_{Salt} (kmol m^{-3})
1.0	LiCl/NaCl/KCl	0.5
1.0	LiCl/KCl	1.0
1.0	LiCl/NaCl/KCl	1.5
1.5	LiCl/NaCl/KCl	0.5
1.5	LiCl/NaCl/KCl	1.0
1.5	LiCl/NaCl/KCl	1.5
2.0	LiCl/NaCl/KCl	0.5
2.0	LiCl/NaCl	1.0
2.0	LiCl/NaCl/KCl	1.5

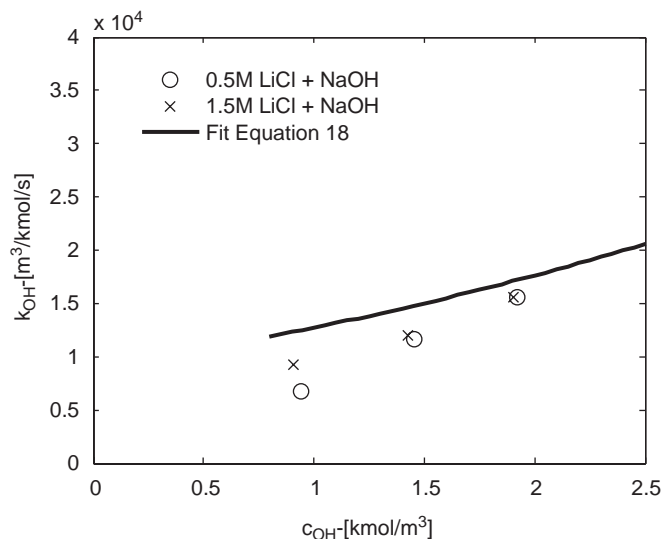


Fig. 3. Dependence of the reaction rate constant on the amount of dissolved LiCl. Kinetic rate constant based on the use of concentrations.

using the traditional approach, i.e. the reaction rate constant is based on the use of concentrations in the kinetic expression. The continuous line in Fig. 3 is the curve for the kinetic rate constant in pure NaOH solutions as obtained using Eq. (18).

As can be seen from Fig. 3 the addition of LiCl generally diminishes the reaction rate constant as compared to a single “pure” NaOH solution, although the diminishing effect of the addition of LiCl is decreasing with a rising hydroxide concentration. This has also been reported in literature where it was stated that the effect of the lithium cation on the reaction rate constant is substantially smaller as compared to the effect of sodium or potassium cations (Nijsing et al., 1959; Pohorecki and Moniuk, 1988).

As can be seen in Fig. 4, the sodium cation indeed has a more distinct effect on the reaction rate constant k_{OH^-} than the lithium ion, and that effect increases with the concentration of sodium ions. At the highest concentration of NaCl added (1.5 M), the reaction rate constant is almost 1.5 times larger compared to the pure NaOH solution.

The effect of adding potassium chloride to a sodium hydroxide solution is even more pronounced than the effect of the addition of sodium chloride (see Fig. 5). In this case the

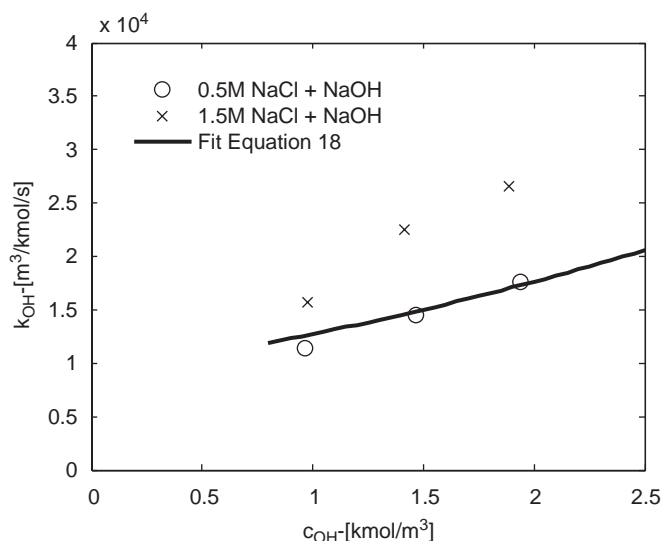


Fig. 4. Dependence of the reaction rate on the amount of dissolved NaCl. Kinetic rate constant based on the use of concentrations.

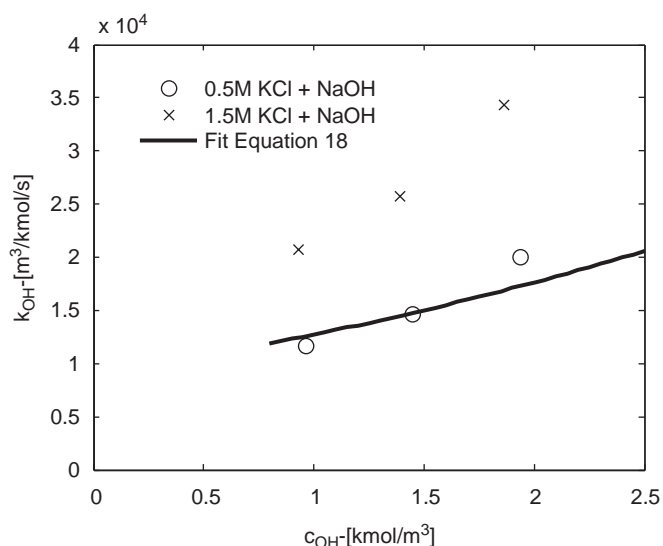


Fig. 5. Dependence of the reaction rate on the amount of dissolved KCl. Kinetic rate constant based on the use of concentrations in the kinetic expression.

reaction rate constant for a 1.5M KCl solution is almost doubled as compared to a pure NaOH solution. This phenomenon is completely in line with the previous findings of Nijsing et al. (1959) and Pohorecki and Moniuk (1988) who reported that the reaction rate constant for the reaction of CO₂ in potassium hydroxide solutions is larger than in sodium hydroxide solutions.

From Figs. 3–5 and Table 5 it can be concluded that it is not possible to arrive at a “constant” rate constant in case only concentrations are used for the description of the reaction rate expression. Moreover, for solutions with identical ionic strength but different added salt, large differences are encountered for the rate constants (see Table 5).

Table 5

Dependence of the reaction rate constant $k_{\text{traditional}}$ on the ionic strength (I)

c_{NaOH} (kmol m ⁻³)	Salt	c_{Salt} (kmol m ⁻³)	I (kmol m ⁻³)	$k_{\text{traditional}} (=k_{\text{OH}^-})$ (m ³ kmol ⁻¹ s ⁻¹)
0.9402	LiCl	0.5	1.4402	6769
0.9650	NaCl	0.5	1.4650	11 377
0.9638	KCl	0.5	1.4638	11 648
1.4528	LiCl	0.5	1.9528	11 621
1.4650	NaCl	0.5	1.9650	14 542
1.4503	KCl	0.5	1.9503	14 570
1.9202	LiCl	0.5	2.4202	15 612
0.9098	LiCl	1.5	2.4098	9297
1.9370	NaCl	0.5	2.4370	17 660
0.9739	NaCl	1.5	2.4739	15 736
1.9363	KCl	0.5	2.4363	20 053
0.9302	KCl	1.5	2.4302	20 869
1.4267	LiCl	1.5	2.9267	11 957
1.4125	NaCl	1.5	2.9125	22 503
1.3937	KCl	1.5	2.8937	25 780
1.9028	LiCl	1.5	3.4028	15 613
1.8850	NaCl	1.5	3.3850	26 593
1.8652	KCl	1.5	3.3652	34 272

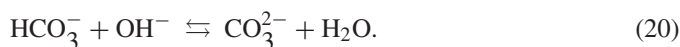
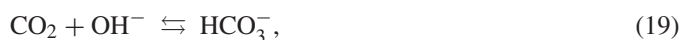
As already proposed by Haubrock et al. (2005) the experiments will be reevaluated with the aid of activity coefficients. Before it is possible to reinterpret the current results using an activity-based approach, first a link between the concentration and the activity must be established. This will be done using the equilibrium model as described in the next section.

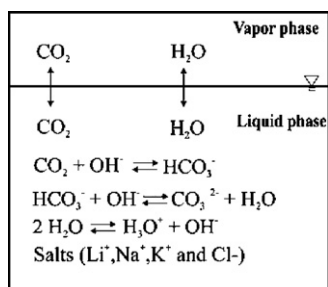
7. Equilibrium model

7.1. Thermodynamic model

In this section the thermodynamic model used in the reinterpretation of the experiments will be described. For the vapor–liquid equilibrium of the system CO₂–NaOH–salt–H₂O it has been assumed that the only species present in the gas phase, are CO₂ and H₂O, respectively. Furthermore, it will be assumed that all salts added are completely dissolved. The model presented here has been implemented in the simulation environment gProms.

In Fig. 6 the system is schematically represented. In the liquid phase CO₂, H₂O, OH⁻ and the products of the chemical reactions as depicted in Fig. 6 are present. The cations stemming from the different salts are not directly taking part in the reaction but influence the reaction rate considerably as shown in the previous section (see Table 5). For the description of the chemical reactions the temperature dependent equilibrium constants of the following reactions are taken into account:



Fig. 6. VLE and chemical reactions in the system CO_2 – NaOH – H_2O –salt.

In the liquid phase the condition for equilibrium as defined according to Rumpf and Maurer (1993) is used

$$K_i^{\text{EQ}} = \prod_{i=1}^3 (a_i^{v_i, \text{EQ}}) = \prod_{i=1}^3 (\gamma_i \cdot m_i)^{v_i, \text{EQ}}. \quad (22)$$

The equilibrium constants for the reactions (19)–(21) together with the material balances for carbon and hydrogen as well as an electro-neutrality balance allow for the unique calculation of the composition of the liquid phase. Activity coefficients in the equilibrium equations are introduced to take the non-ideality of the liquid phase into account. The material balances applied in this model are as follows:

$$\text{carbon-balance: } n_{\text{CO}_2}^0 = n_{\text{CO}_2} + n_{\text{HCO}_3^-} + n_{\text{CO}_3^{2-}}, \quad (23)$$

hydrogen-balance:

$$2 \cdot n_{\text{H}_2\text{O}}^0 + n_{\text{OH}^-}^0 = 2 \cdot n_{\text{H}_2\text{O}} + n_{\text{OH}^-} + n_{\text{HCO}_3^-} + 3 \cdot n_{\text{H}_3\text{O}^+}. \quad (24)$$

The electro-neutrality balance gives

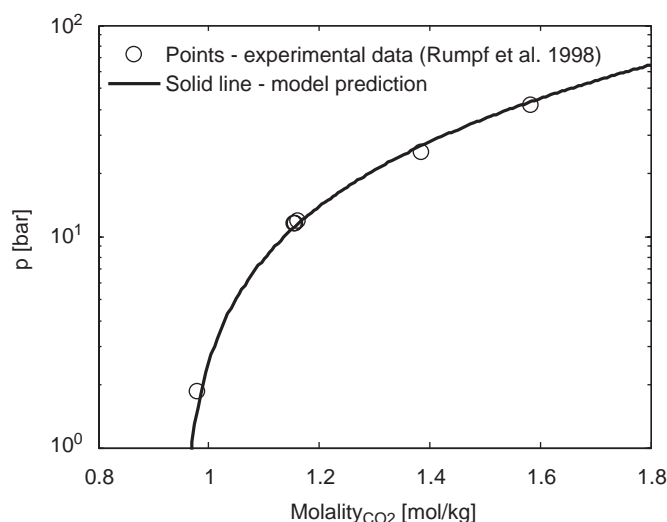
$$n_{\text{OH}^-} + n_{\text{HCO}_3^-} + 2 \cdot n_{\text{CO}_3^{2-}} + n_{\text{Cl}^-} - n_{\text{H}_3\text{O}^+} - n_{\text{Na}^+} - n_{\text{Salt, cation}^+} = 0. \quad (25)$$

The phase equilibrium for water and carbon dioxide is described with the subsequent equations

$$p \cdot y_w \cdot \phi_w'' = p_w^s \cdot \phi_w^s \cdot a_w \cdot \exp\left(\frac{v_w \cdot (p - p_w^s)}{R \cdot T}\right), \quad (26)$$

$$p \cdot y_{\text{CO}_2} \cdot \phi_{\text{CO}_2}'' = H_{\text{CO}_2, w}^m(T, p_w^s) \cdot m_{\text{CO}_2} \cdot \gamma_{\text{CO}_2}^* \exp\left(\frac{v_{\text{CO}_2, w}^\infty \cdot (p - p_w^s)}{R \cdot T}\right). \quad (27)$$

As it can be seen from the above listed equations the model requires the knowledge of a number of parameters like the equilibrium constants K_1^{EQ} to K_3^{EQ} , the activities γ_i^* of all species in the liquid phase, Henry's constant for carbon dioxide dissolved in pure water ($H_{\text{CO}_2, w}^m$), the vapor pressure (p_w^s), the molar volume (v_w) of pure water and the partial molar volume ($v_{\text{CO}_2, w}^\infty$) of carbon dioxide, as well as information on the fugacity coefficients ϕ_w'' and ϕ_{CO_2}'' in the gas phase. These parameters and their values are discussed in Appendix A.

Fig. 7. Comparison of experimental data with the VLE model of CO_2 – NaOH – H_2O .

It should be noted that the developed VLE model has not been experimentally validated as there is a lack of experimental VLE data. Nevertheless, the VLE model where only sodium hydroxide and CO_2 are present has been validated with data taken from Rumpf et al. (1998). The current thermodynamic model predicts the experimentally determined overall pressures within an error of 6% if low pressure values (< 1 bar) are excluded (Fig. 7).

However, the deviation in terms of the predicted pressure at low loadings (low pressures) can be significant (up to 45%). Nevertheless, in the low loading region the activity coefficients as predicted by the model—being the actual parameters needed in the interpretation of the absorption rate experiments—are not showing a significant different behavior than in the high loading regime (see Haubrock et al., 2005 for a comparison).

This means that the current prediction of the activity coefficients for CO_2 and OH^- is considered to be sufficiently accurate to be used in the kinetic expression for at least “pure” NaOH solutions.

It might be expected that the error in terms of VLE data is larger for mixed electrolyte systems than for the “simple” sodium hydroxide– CO_2 system. One reason leading to this assumption is that for NaOH /salt solutions more interaction parameters are needed than for a NaOH solution alone, and, moreover, not all required interaction parameters are stemming from the same literature source (especially for solutions containing LiCl). This might introduce errors in the predicted values of the activity coefficients of CO_2 and OH^- which are difficult to quantify at this stage.

8. Experimental results and their interpretation using the activity-based approach

In Section 6 the experimental absorption rate data have been interpreted using the conventional approach, i.e. using “only” concentrations in the reaction rate expression. That section

showed that there is a substantial influence of the kind of cations being present in the solution and the concentration of the cations on the reaction rate constant, respectively.

In this section the experimental results will be reinterpreted using the activity coefficients of the reacting species in the reaction rate expression.

From a fundamental thermodynamic point of view the kinetics of reaction 1 should be written in terms of activities to be consistent with the activity-based equilibrium constant (see Eq. (22)). The suggested reaction rate equation for the forward reaction of CO_2 and OH^- to HCO_3^- is thus written as follows:

$$r^m = k_{\text{OH}^-}^m(\gamma) \cdot a_{\text{CO}_2} \cdot a_{\text{OH}^-}, \quad (28)$$

where the activity a_{CO_2} is equal to the product $m_{\text{CO}_2} \gamma_{\text{CO}_2}$ and the activity a_{OH^-} is equal to $m_{\text{OH}^-} \gamma_{\text{OH}^-}$, respectively. To obtain the activity-based reaction rate constants the values as derived for the concentration-based rate expression can be used. The relation between the two of them can be shown to be (see Appendix B for derivation):

$$k_{\text{OH}^-}^m(\gamma) = \frac{k_{\text{OH}^-}}{\gamma_{\text{OH}^-} \gamma_{\text{CO}_2}} \times \frac{\rho^2}{(\rho - \sum_{\text{all ions } i} c_i M_i)(1 + \sum_{\text{all ions } i} m_i M_i)^2}. \quad (29)$$

Applying Eq. (28) is supposed to have two advantages compared to the traditional concentration-based rate expression. Firstly, the change of the solution density (especially at a higher ionic strength) is accounted for by using molalities instead of density dependent concentrations. Secondly, it is expected that the introduction of activity coefficients in the reaction rate equation will diminish the influence of the different ions on the reaction rate constant and moreover the dependence of the reaction rate constant on the ionic strength.

The results of applying the activity-based approach and the traditional approach to the system $\text{NaOH-CO}_2\text{-water}$ is shown in Fig. 8 (see also Haubrock et al., 2005).

For the $\text{NaOH-CO}_2\text{-water}$ system the difference between molalities and concentrations in the applied range of concentrations was always less than 1% therefore in Fig. 8 it has been decided to use concentrations as the x -coordinate for the sake of simplicity. The black solid line is representing the kinetic rate constant for the pure NaOH system according to the activity-based approach and will be used in the following figures as a reference to assess the results for the $\text{NaOH-CO}_2\text{-salt-water}$ system. The activity-based reaction rate constant has a value of approximately $16\,500 \text{ kg kmol}^{-1} \text{ s}^{-1}$ and is nearly constant for sodium hydroxide concentrations between 1 and 3 kmol m^{-3} (see Fig. 8).

From Fig. 8 it can be concluded that the use of activity-based kinetics indeed results in a near constant rate constant. However, it must be noted that at lower values of the ionic strength the value of the rate constant is somewhat lower ($< 10\%$). This deviation can probably be attributed on the one hand to uncertainties in the physical parameters used in the interpretation

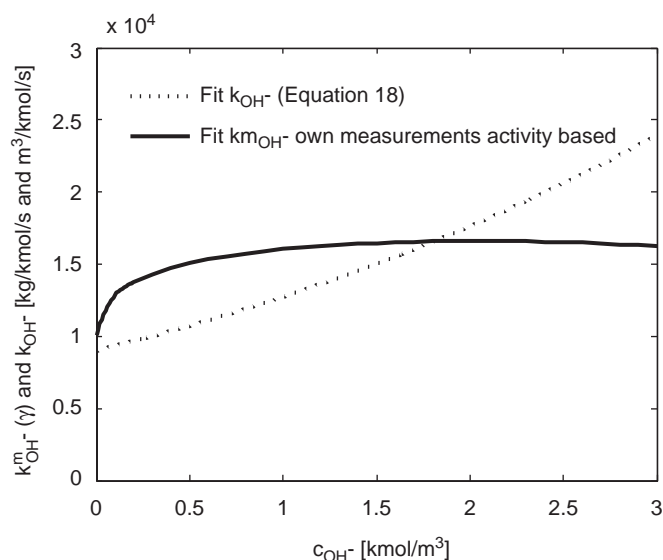


Fig. 8. Comparison between the kinetic constant derived with the traditional approach and the activity-based approach for the system $\text{NaOH-CO}_2\text{-water}$.

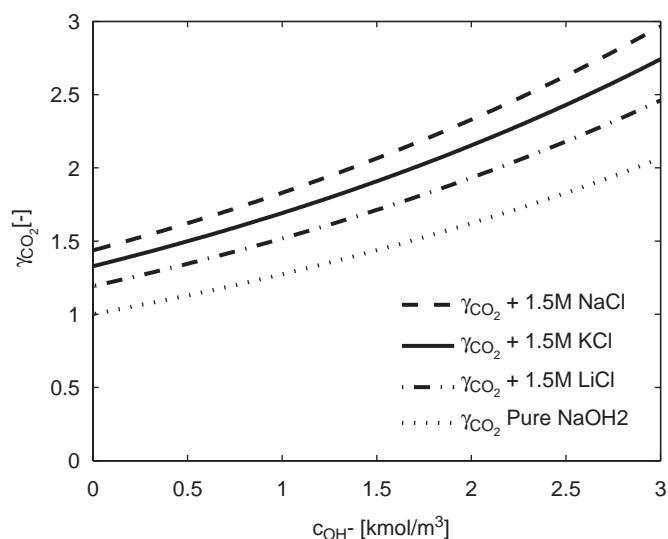


Fig. 9. Activity coefficients of CO_2 as a function of the hydroxide concentration.

of the experiments and on the other hand on the use of the presently developed equilibrium model which is used to estimate the required activity coefficients.

The values of the activity coefficients of CO_2 and the OH^- anion according to the Pitzer equilibrium model (Section 7) are shown in Figs. 9 and 10. The activity coefficients are plotted for the systems NaOH-LiCl , NaOH-NaCl and NaOH-KCl . For a comparison the activity coefficients of a pure NaOH solution are also shown.

In case of a pure NaOH solution the activity coefficient of OH^- steeply decreases from unity until a hydroxide concentration of 0.5 M and then increases slightly again. This behavior cannot be observed for the other solutions. This is due to the

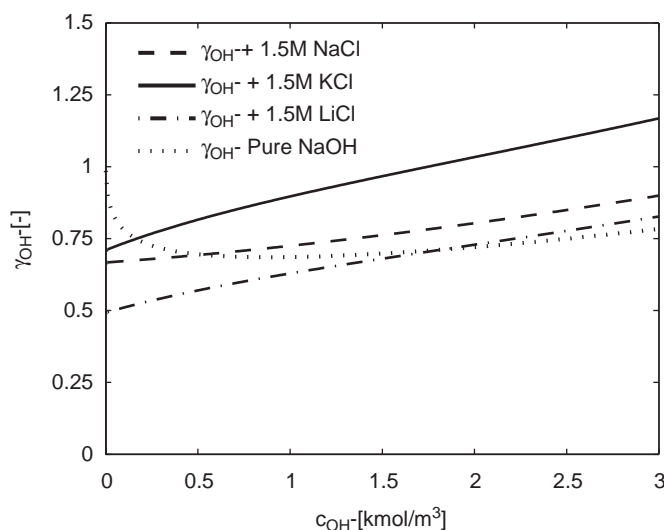


Fig. 10. Activity coefficients of OH^- as a function of the hydroxide concentration.

fact that the ionic strength is equal to zero for a pure sodium hydroxide solution at an hydroxide molality of zero (i.e. water) whereas the doped solutions already contain 1.5 mol kg^{-1} salt at a hydroxide concentration of zero. Hence, the ionic strength of the doped solutions is well above zero and therefore the course of the OH^- activity coefficient of pure NaOH is different from the others.

It can be clearly seen that the activity coefficients of OH^- are well below unity for mixtures containing LiCl and NaCl whereas the activity coefficient of the KCl containing mixture is slightly above unity. The activity coefficients of CO_2 for all three salt mixtures are starting at values above unity and do substantially increase with rising hydroxide concentration.

The activity coefficient of CO_2 in the three doped solutions has a larger value at a hydroxide molality of zero. This fact can be attributed to the higher ionic strength of the doped solutions. Nevertheless the shape of the curves is not altered by the unequal ionic strength. Looking at the structure of the equations used in the Pitzer approach (see Rumpf et al., 1998) and keeping in mind that “only” the interaction parameter β_0 (see Table A5) is employed to calculate the activity coefficients of CO_2 , it could be expected that the shape of the curve would barely change.

The CO_2 and OH^- activity coefficients of the mixture containing LiCl are clearly below the values for the mixtures containing NaCl and KCl salts, respectively. Nevertheless, the dependency of the activity coefficients of CO_2 and OH^- on the hydroxide concentration seems to be the same for all three salts.

As it can be seen in Section 6 the influence of the addition of LiCl to the caustic solution on the reaction rate constant is least pronounced if compared to the two other salts, i.e. NaCl and KCl. This was also expected as in pure lithium hydroxide solutions only a limited effect of the LiOH concentration on the reaction rate constant was observed (Pohorecki and Moniuk, 1988). In the following the impact of using activ-

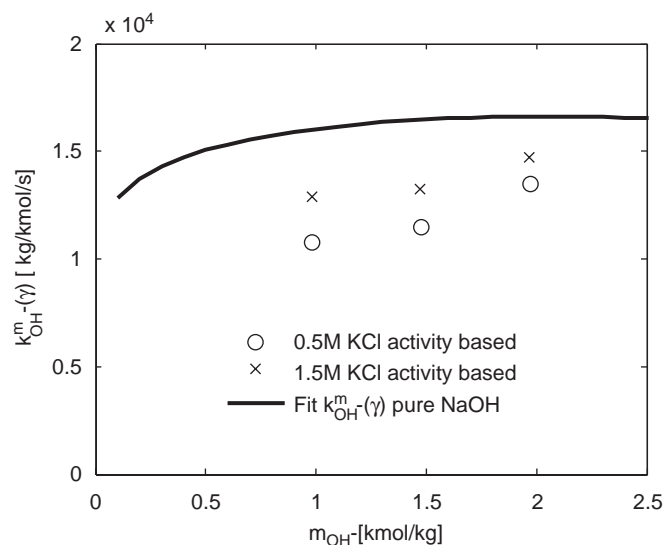


Fig. 11. Comparison of the reaction rate constant using the new approach for NaOH solutions with added KCl in a molarity of 0.5 and 1.5 KCl (see also Fig. 5).

ity coefficients in the reaction rate equation will be presented. First the effect of using activities for the most non-ideal system containing potassium chloride will be shown; subsequently the three hydroxide–salt solutions will be compared among each other.

In Fig. 11 the values of the activity-based reaction rate constant for two different potassium chloride concentrations are depicted. When compared to Fig. 5 (showing the concentration-based kinetic rate constant) it can be clearly seen that the influence of the potassium chloride concentration is dramatically decreased and the absolute values of the reaction rate constants for both potassium chloride concentrations are relatively close to each other and also close to the “new” reinterpreted reaction rate constant for pure NaOH solutions. Furthermore, the absolute value of $k_{\text{OH}^-}^m(\gamma)$ is only slightly ($< 20\%$) increasing with the hydroxide concentration for both KCl concentrations and also for a “pure” NaOH solution.

As previously shown in Figs. 4 and 5 the values of the “traditional” reaction rate constant with added sodium chloride and potassium chloride are increasing with rising hydroxide concentration and the absolute values are all substantially higher than those for the pure sodium hydroxide solution. Furthermore, the values of the reaction rate constant for the caustic sodium and potassium chloride solutions are diverging from each other with rising hydroxide concentration.

Applying activity coefficients in the reaction rate expression considerably reduces the dependence of the reaction rate constant on the ionic strength as shown in Fig. 12. The activity-based values of the reaction rate constant $k_{\text{OH}^-}^m(\gamma)$ differ—in the investigated sodium hydroxide concentration range and for 1.5 M KCl or NaCl—less than 15% and 20% among each other, respectively.

The activity-based reaction rate constant has a value of approximately $16500 \text{ kg kmol}^{-1} \text{ s}^{-1}$ and is nearly constant for

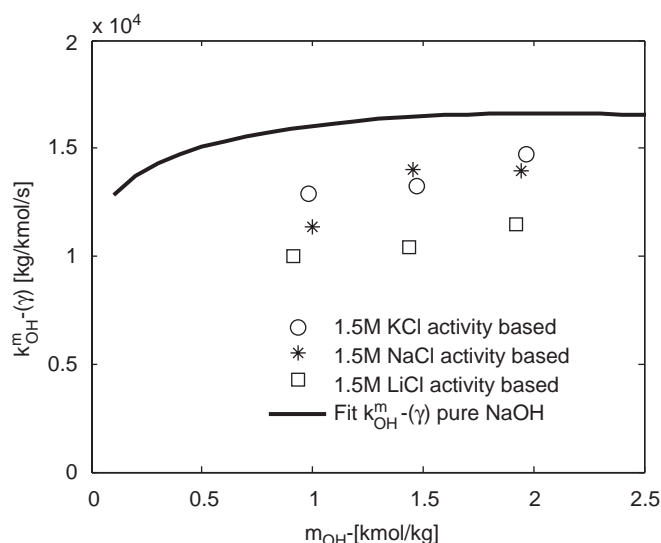


Fig. 12. Comparison of the reaction rate constant using the traditional and new approach for NaOH solutions with various salts added to it in a concentration of 1.5 M.

sodium hydroxide concentrations between 1 and 3 kmol kg⁻¹ (see Fig. 8). With the exception of the activity based reaction rate constant $k_{\text{OH}^-}^m(\gamma)$ of LiCl doped solutions, the $k_{\text{OH}^-}^m(\gamma)$ values of KCl and NaCl doped solutions deviate only 20% and 30% from the average $k_{\text{OH}^-}^m(\gamma)$ value of a the pure sodium hydroxide solution, respectively.

Moreover, by applying activity coefficients in the calculation of the reaction rate constant it is possible to compensate almost completely for the increase of the reaction rate constant with an increasing sodium hydroxide concentration. As can be seen from Fig. 12 this holds for all three doped sodium hydroxide solutions as the value of the activity-based reaction rate constant of one particular solution is nearly unchanged over the investigated sodium hydroxide concentration range.

As can be seen from Fig. 12, the absolute values of the “new” reaction rate constant for the sodium and sodium–potassium salt solutions are merging to the same line—slightly below the pure NaOH line—if activity coefficients are applied in the reaction rate expression. Hence, the application of activity coefficients in the reaction rate expression seems to reduce both the dependence of the reaction rate constant on the hydroxide concentration and on the type and concentration of cations being present in the solution.

In Fig. 13 the activity-based approach of hydroxide–salt solutions is compared to the “base case” where CO₂ is only absorbed in a sodium hydroxide solution.

This parity plot again clearly shows that the effect of adding the salts NaCl and KCl to NaOH can be well accounted for by introducing activity coefficients in the reaction rate constant. In case of LiCl doped NaOH solutions the result is still fair (within 40%) whereas it should be mentioned that the offset between the results for a LiCl doped solution and KCl/NaCl doped solutions seems to be systematic and near constant. Taking into account the fact that the kinetic constant for solutions where

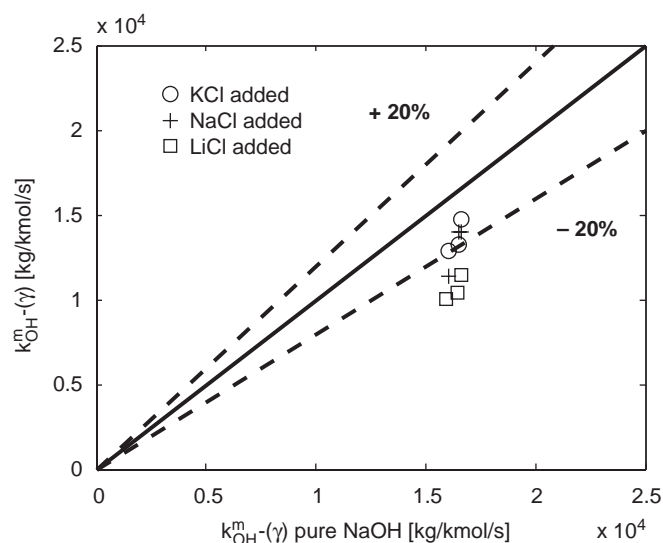


Fig. 13. Parity plot: comparison of the activity-based rate constants of pure NaOH and NaOH solutions containing the specified salts.

either sodium or potassium ions are present have substantially higher reaction rates—a factor 2 (NaCl) and a factor 2.5 (KCl) at 2 mol l⁻¹ NaOH and 1.5 mol l⁻¹ salt, respectively—the application of activity coefficients in the reaction rate equation reduces the influence on the cations and the ionic strength considerably (see Fig. 13).

The remaining difference (see Figs. 12 and 13) in the absolute values of the reaction rate constant might be explained with the accuracy of some input data:

- The activity coefficients needed for the calculation of the activities may be inaccurate. As an example of this, the interaction parameters for lithium have been taken from several different sources and it is likely that this will introduce errors.
- Furthermore, the diffusion coefficients have been assumed to be reciprocally proportional to the viscosities of the salt (see Eq. (14)). Hence, the diffusion coefficient does strongly depend on the viscosities whereas if e.g. a modified Stokes–Einstein relation would have been used (using an exponent of 0.8; van Swaaij and Versteeg, 1992), this influence would have been lower. Using the modified Stokes–Einstein relationship would have resulted in lower values of the kinetic rate constant.
- The physical solubility of CO₂ has been determined using Schumpe’s method. A preliminary comparison with experimentally derived CO₂ solubilities (based on the use of the N₂O analogy) shows that this method might introduce errors in this parameter of approximately 20%.

A further reduction or elimination of these uncertainties will probably yield even better results for the new kinetic approach (i.e. further reduce the influence of the NaOH concentration on the kinetic rate constant for “pure” NaOH solutions and further close the gap between the kinetic rate constants as observed for NaOH solutions with different added salts).

However, a further elimination or reduction of the remaining uncertainties of the input data requires various complete new and extensive studies and is therefore beyond the scope of this paper. The input data as used in the evaluation of the experimental absorption rate experiments have shown to be sufficiently accurate to be able to show the potential of the new kinetic approach.

9. Conclusions

In this study it has been shown that the kinetics of CO₂ and OH[−] in aqueous salt-solutions can be reasonably described with a single kinetic rate constant, if this constant has been determined using an activity-based kinetic rate expression. Both, the influence of the hydroxide concentration and the concentration of the additionally added salt on the kinetic rate constant, were reduced significantly as compared to the kinetic rate constants using the traditional, concentration-based, approach. The reaction rate constant $k_{\text{OH}^-}^m(\gamma)$ derived using an activity-based approach was calculated to be $12500 \pm 2000 \text{ kg kmol}^{-1} \text{ s}^{-1}$. This relatively small range in the kinetic rate constant is remarkable compared to the traditional concentration-based approach where a huge (up to a factor of ~ 4) difference between the reaction rate constants can be observed.

This means that in the activity-based approach, the reaction rate constant is much more a real constant compared to the traditional approach. The scatter of the “new” reaction constant which can still be observed might be attributed to errors in the required chemical/physical input data used in the evaluation of the experimental data as e.g. the diffusion coefficients, physical solubility data and the interaction parameters needed for the determination of the activity coefficients.

Still, overall it seems that the new approach incorporating activities in the reaction rate expression is well suited to represent the kinetics of a non-ideal system as currently studied, and may also be suited to describe other non-ideal systems. Besides giving a uniform reaction rate constant, there is another profound reason to apply this method, especially so for reactive systems operated close to equilibrium. This is because, in the new approach non-idealities are not lumped in the reaction rate constant which makes the formulation of the kinetics, over the entire conversion range, consistent with the thermodynamically sound formulation of the chemical equilibrium, where also activities are employed.

Therefore, the application of the new methodology is thought to be very beneficial especially in processes where “the thermodynamics meet the kinetics”. Hence, it is anticipated that the new kinetic approach will firstly find its major application in the modeling of integrated processes like Reactive Distillation, Reactive Absorption and Reactive Extraction where both, thermodynamics and kinetics, are of essential importance and activity coefficients deviate substantially from ideal behavior.

Notation

a	liquid phase activity, kmol kg^{-1}
A_ϕ	Debye–Hueckel parameter
A	area, m^2
$B_{\text{CO}_2, w}$	mixed virial coefficient CO ₂ –water, $\text{cm}^{-3} \text{ mol}$
c	concentration, kmol m^{-3}
C_ϕ	third virial coefficient in Pitzer’s model, Pa or bar
D	relative dielectric constant of water
e	proton charge, C
H_{CO_2}	Henry’s constant in the thermodynamic model, MPa kg mol^{-1}
He	Henry’s constant, $\text{Pa m}^3 \text{ mol}^{-1}$
I	ionic strength, kmol m^{-3}
J_{CO_2}	flux, $\text{mol s}^{-1} \text{ m}^{-2}$
k	Boltzmann’s constant, J K^{-1}
k_1	pseudo-first-order reaction rate constant, s^{-1}
$k_{\text{OH}^-}^{\text{OH}^-}$	second-order reaction rate constant, $\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$
$k_{\text{OH}^-}^{\text{inf}}$	second-order reaction rate constant at infinite dilution, $\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$
$k_{\text{OH}^-}^m(\gamma)$	second-order reaction rate constant activity based, $\text{kg kmol}^{-1} \text{ s}^{-1}$
k_L	mass transfer coefficient, m s^{-1}
K_i^{EQ}	chemical equilibrium constant, $[-]$ or kg mol^{-1}
m_i	molality of species i , mol kg^{-1}
$m_{i,j}$	dimensionless solubility of a gas i in a solution (solvent) j
mass_i	mass of component i , kg
M_i	molar mass, kg mol^{-1}
n	mole of substance, mol
N_A	Avogadro’s number
p	pressure, MPa
P_1	Fit parameter 1 in Eq. (18), $\text{kmol}^2 \text{ m}^{-6}$
P_2	Fit parameter 2 in Eq. (18), kmol m^{-3}
r	second-order reaction rate, $\text{kmol m}^{-3} \text{ s}^{-1}$
r^m	second-order reaction rate molality based, $\text{kmol kg}^{-1} \text{ s}^{-1}$
R	universal gas constant, $\text{J mol}^{-1} \text{ K}^{-1}$
T	temperature, K
v	partial molar volume, $\text{cm}^3 \text{ mol}^{-1}$
V	volume, m^3
y	mole fraction in the gas phase
z	number of charges

Greek letters

$\beta_{i,j}$	second virial coefficient, $\text{cm}^3 \text{ mol}^{-1}$
γ	activity coefficient
ϵ_0	vacuum permittivity, $\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$
μ	dynamic viscosity, Pa s^{-1}
ν_i	stoichiometric coefficient
ν	kinematic viscosity, $\text{m}^2 \text{ s}^{-1}$
ρ	density, kg m^{-3}
$\tau_{i,j,k}$	ternary interaction parameter
ϕ	fugacity

Superscripts and subscripts

EQ	equilibrium
<i>i</i>	component <i>i</i> or index
interface	phase interface liquid–gas
<i>j</i>	component <i>j</i> or index
<i>k</i>	component <i>k</i> or index
<i>m</i>	molality scale
<i>s</i>	saturated
<i>w</i>	water
∞	at infinite dilution or infinite
0	initial value
"	gas phase
*	normalized to infinite dilution

Acknowledgments

The authors gratefully acknowledge the financial support of Shell Global Solutions. Also, H.F.G. Moed is acknowledged for the construction of the experimental setup and S.F.P. ten Donkelaar for his part in the experimental work.

Appendix A. Parameters used in the equilibrium model incorporating the Pitzer model

The temperature-dependent equilibrium constant for water was taken from Edwards et al. (1978) whereas the equilibrium constants for the other two reactions have been taken from Kawazuishi and Prausnitz (1987) (see Table A1).

Henry's constant for the solubility of CO₂ in water was taken from Rumpf and Maurer (1993) (see Table A2). The value of the Henry's constant at 298 K was compared to the one measured by Versteeg and Vanswaaij (1988) which showed that the deviation between the two constants was less than 3%.

Saul and Wagner (1987) was used to provide the equations for the vapor pressure and the molar volume of pure water. The fugacity coefficients were calculated with the virial equation of state truncated after the second virial coefficient. The second virial coefficients of water and carbon dioxide were calculated from correlations based on data from Dymond and Smith (1980) (see Table A3). The mixed virial coefficient $B_{\text{CO}_2,w}$ was taken from Hayden and O'Connell (1975) (see Table A4). The partial molar volume of carbon dioxide dissolved in water at infinite dilution $v_{\text{CO}_2,w}^\infty$ was calculated according to the method of Brelvi and O'Connell (1972) (see Table A4).

The activity coefficients in the liquid phase were calculated with Pitzer's equation for the Gibbs energy of an electrolyte solution (Pitzer, 1973). The semi-empirical Pitzer model has been successfully applied by a number of authors (Engel, 1994; Rumpf et al., 1998; van der Stegen et al., 1999) for the description of different electrolyte systems.

Interactions between ions and neutral molecules can also be considered in the extended Pitzer model which is important for systems where neutral molecules are dissolved in electrolyte solutions as e.g. CO₂ in caustic solutions. A general shortcoming of the Pitzer model is that its application is restricted to the aqueous solutions (Pitzer, 1991), however, in the present

Table A1

Equilibrium constants for chemical reactions (based on activities) $\ln K_i^{\text{EQ}} = A_i/(T[K]) + B_i \ln(T[K]) + C_i(T[K]) + D_i$

Equilibrium constant	A	B	C	D
K_1^{EQa} (reaction 19)	5719.89	7.97117	−0.0279842	−38.6565
K_2^{EQa} (reaction 20)	4308.64	4.36538	−0.0224562	−24.1949
K_3^{EQb} (reaction 21)	−13 445.9	−22.4773	0	140.932

^aKawazuishi and Prausnitz (1987).

^bEdwards et al. (1978).

Table A2

Henry's constant for the solubility of carbon dioxide in pure water $\ln H_{\text{CO}_2,w} [\text{MPa} \cdot \text{kg} \cdot \text{mol}^{-1}] = A_{\text{CO}_2,w} + B_{\text{CO}_2,w}/T[K] + C_{\text{CO}_2,w}(T[K]) + D_{\text{CO}_2,w} \ln(T[K])$

	$A_{\text{CO}_2,w}$	$B_{\text{CO}_2,w}$	$C_{\text{CO}_2,w}$	$D_{\text{CO}_2,w}$	Reference
$H_{\text{CO}_2,w}$	192.876	−9624.4	0.01441	−28.749	Rumpf and Maurer (1993)

Table A3

Pure component second virial coefficients ($273 \leq T[K] \leq 473$) $B_{i,i} [\text{cm}^3 \cdot \text{mol}^{-1}] = a_{i,i} + b_{i,i} \cdot (c_{i,i}/T[K])^{(d_{i,i})}$

<i>i</i>	$a_{i,i}$	$b_{i,i}$	$c_{i,i}$	$d_{i,i}$	Ref.
CO ₂	65.703	−184.854	304.16	1.4	— ^a
H ₂ O	−53.53	−39.29	647.3	4.3	— ^a

^aDymond and Smith (1980).

Table A4

Mixed second virial coefficients and partial molar volumes

<i>T</i> [K]	$B_{\text{CO}_2,w}$ (cm ³ mol ^{−1})	Ref.	$v_{\text{CO}_2,w}^\infty$ (cm ³ mol ^{−1})	Ref.
313.15	−163.1	— ^a	33.4	— ^b
333.15	−144.6	— ^a	34.7	— ^b
353.15	−115.7	— ^a	38.3	— ^b
373.15	−104.3	— ^a	40.8	— ^b
393.15	−94.3	— ^a	43.8	— ^b
413.15	−85.5	— ^a	47.5	— ^b

^aHayden and O'Connell (1975).

^bBrelvi and O'Connell (1972).

study this is not a limitation as attention is focused on the CO₂–NaOH–H₂O–salt system.

An outstanding property of Pitzer's model is the ability to predict the activity coefficients in complex electrolyte solutions from data available for simple subsystems. This avoids the use of triple or quadruple interaction parameters which are very scarcely reported in the open literature whereas for the most common single electrolytes binary interaction parameters are readily available. In the extended Pitzer equation, which is described in more detail by Rumpf et al. (1998), the ion–ion binary interaction parameters $\beta_{i,j}^0$ and $\beta_{i,j}^1$ as well as the ternary interaction parameter $\tau_{i,j,k}$ are characteristic for each aqueous single electrolyte solution. These parameters are solely determined by the properties of the pure electrolytes.

In the liquid phase the reactions (19)–(21) take place. For the computation of the equilibrium constants K_i^{EQ} the activity

Table A5

Ion–ion interaction parameters incorporated in the model (at 25 °C)

Interaction	$10^2 \cdot (\beta^0, \lambda)$ (kg mol ⁻¹)	$10 \cdot \beta^1$ (kg mol ⁻¹)	$10^3 \cdot C^\phi$ (kg ² mol ⁻²)	Ref.
Na ⁺ –OH ⁻	+8.64	+2.53	+4.40	Pitzer and Peiper (1982)
Na ⁺ –HCO ₃ ⁻	+2.80	+0.44	0	Pitzer and Peiper (1982)
Na ⁺ –CO ₃ ²⁻	+3.62	+15.1	+5.2	Pitzer and Peiper (1982)
Na ⁺ –Cl ⁻	+7.65	+2.664	+1.27	Zemaitis et al. (1986)
CO ₂ –Na ⁺	+12.8	–	–	Pitzer and Peiper (1982)
K ⁺ –OH ⁻	+12.98	+3.20	+4.1	Roy et al. (1984)
K ⁺ –HCO ₃ ⁻	–1.07	+0.48	0	Roy et al. (1984)
K ⁺ –CO ₃ ²⁻	+12.88	+14.33	+0.5	Roy et al. (1987)
K ⁺ –Cl ⁻	+4.835	+2.122	+0.84	Zemaitis et al. (1986)
CO ₂ –K ⁺	+9.46			Engel (1994)
Li ⁺ –OH ⁻	+1.5	1.4	–	Zemaitis et al. (1986)
Li ⁺ –HCO ₃ ⁻	No data available			
Li ⁺ –CO ₃ ²⁻	–38.934	–22.737	–162.859	Deng et al. (2002)
Li ⁺ –Cl ⁻	+14.94	+3.074	+3.59	Zemaitis et al. (1986)
CO ₂ –Li ⁺	+5.8	–	–	Schumpe (1993)

coefficients of the following species were evaluated with the Pitzer model: CO₂, OH⁻, HCO₃⁻, CO₃²⁻ and H₃O⁺.

For the sodium hydroxide–CO₂–salt the Pitzer interaction parameters applied in the Pitzer model as used in this study will be discussed.

In the Pitzer model, as well as in other electrolyte models (i.e. electrolyte NRTL) (Zemaitis et al., 1986), interactions between neutral molecules as well as interactions between neutral molecules and anions (i.e. Cl⁻, OH⁻ in this study) are neglected. Therefore, interactions between neutral molecules (CO₂, water) as well as interactions between the anions in the present system and the neutral molecules have not been taken into account in the form of interaction parameters.

Parameters describing interactions between charged species in the system CO₂–sodium hydroxide–water–salt have been taken from Pitzer and Peiper (1982). On the basis of expected relative concentrations of the various components in the solution, the ion–ion interactions listed in Table A5 are foreseen to be significant. These interaction parameters have been incorporated as the ions or molecules will be present in high concentrations in the solution. It is anticipated that the interactions between these species account for a large extent for the non-idealities in the solution.

Parameters describing interactions between the molecule carbon dioxide and charged species have been considered as follows: for the interaction between carbon dioxide and salt cations (Li, Na, K) the parameters as given in Table A5 were used. Interactions between carbon dioxide and dissolved bicarbonate or carbonate have been omitted as those interactions are reported to be negligible (Edwards et al., 1978; Pawlikowski et al., 1982). Due to the low concentration of H₃O⁺ ions in the caustic solutions, all interaction parameters between this component and CO₂ have been set to zero.

The addition of different salts to the system CO₂–NaOH–H₂O influences the activity coefficients of all the components in the system. The Pitzer interaction parameters that have been considered in the different CO₂–NaOH–H₂O–salt systems and

those which are needed for the calculation of the activities are summarized in Table A5.

As can be seen in Table A5 all required interaction parameters for the systems of interest in the present study are available in literature. The possible effect of temperature on the interaction parameters has been assumed to be negligible. This basically corresponds to the assumption that the temperature effect on the activity coefficient is the same for each component (Engel, 1994). The dielectric constant of pure water as used in the Pitzer model was taken from Horvath (1985).

In the Pitzer model only binary interaction parameters have been taken into account as ternary interaction parameters are only scarcely reported in literature, especially for the mixed electrolyte systems as used in this study. Therefore, ternary interaction parameters have been disregarded to prevent the possible introduction of more inconsistencies in the model.

Already at this point it can be stated that to further improve the accuracy of the Pitzer model for the predictions of activity coefficients of CO₂ and OH⁻ in solutions as investigated in this study, it seems necessary to carry out additional VLE-experiments, especially at low partial pressures of CO₂ and low CO₂ loadings. This would yield more reliable interaction parameters for the systems of interest in this study and hence more precise values of the required activity coefficients. As this was not the scope of the present study these experiments have not been carried out at this stage.

Appendix B. Derivation of equations used in the activity-based kinetic approach

B.1. Conversion between molalities and concentrations of mixed salt solutions

The concentration and the molality of hydroxide ions can be expressed as follows:

$$c_{\text{OH}^-} = \frac{\text{mass}_{\text{OH}^-}}{M_{\text{OH}^-} \cdot V} \quad (\text{B.1})$$

$$m_{\text{OH}^-} = \frac{\text{mass}_{\text{OH}^-}}{M_{\text{OH}^-} \cdot \text{mass}_{\text{solvent}}} \rightarrow \text{mass}_{\text{OH}^-} \\ = m_{\text{OH}^-} \cdot M_{\text{OH}^-} \cdot \text{mass}_{\text{solvent}}. \quad (\text{B.2})$$

Combining Eqs. (B.1) and (B.2) gives

$$c_{\text{OH}^-} = \frac{\text{mass}_{\text{OH}^-}}{M_{\text{OH}^-} \cdot V} = \frac{m_{\text{OH}^-} \cdot M_{\text{OH}^-} \cdot \text{mass}_{\text{solvent}}}{M_{\text{OH}^-} \cdot V} \\ = \frac{\text{mass}_{\text{solvent}} \cdot m_{\text{OH}^-}}{V}. \quad (\text{B.3})$$

The volume of a mixed salt solution can be expressed as

$$V = \frac{\text{mass}}{\rho} = \frac{\text{mass}_{\text{solvent}} + \sum_{\text{all ions } i} m_i \cdot \text{mass}_i}{\rho} \\ = \frac{\text{mass}_{\text{solvent}} + \text{mass}_{\text{solvent}} \sum_{\text{all ions } i} m_i M_i}{\rho} \\ = \frac{\text{mass}_{\text{solvent}} (1 + \sum_{\text{all ions } i} m_i M_i)}{\rho}. \quad (\text{B.4})$$

This yields:

$$c_{\text{OH}^-} = \frac{\rho m_{\text{OH}^-}}{1 + \sum_{\text{all ions } i} m_i M_i}. \quad (\text{B.5})$$

Rearranging the last formula yields the conversion from concentration to molality

$$m_{\text{OH}^-} = \frac{c_{\text{OH}^-} (1 + \sum_{\text{all ions } i, i \neq \text{OH}^-} m_i M_i)}{\rho - c_{\text{OH}^-} M_{\text{OH}^-}}. \quad (\text{B.6})$$

B.2. Relation between the activity-based rate constant and the concentration-based rate constant

The activity-based reaction rate reads as follows:

$$r^m = k_{\text{OH}^-}^m(\gamma) a_{\text{CO}_2} a_{\text{OH}^-} \\ = k_{\text{OH}^-}^m(\gamma) \gamma_{\text{CO}_2} \gamma_{\text{OH}^-} m_{\text{CO}_2} m_{\text{OH}^-} (\text{mol kg}_{\text{solvent}}^{-1} \text{s}^{-1}). \quad (\text{B.7})$$

The concentration-based reaction rate can be written as

$$r = k_{\text{OH}^-} c_{\text{CO}_2} c_{\text{OH}^-} (\text{kmol m}^{-3} \text{s}^{-1}). \quad (\text{B.8})$$

Replacing concentrations by molalities in Eq. (B.8) by using Eq. (B.5) yields:

$$r = k_{\text{OH}^-} \frac{\rho^2 m_{\text{OH}^-} m_{\text{CO}_2}}{(1 + \sum_{\text{all ions } i} m_i M_i)^2}. \quad (\text{B.9})$$

From Eq. (B.7) it can be derived that

$$m_{\text{OH}^-} m_{\text{CO}_2} = \frac{r^m}{k^m(\gamma) \gamma_{\text{OH}^-} \gamma_{\text{CO}_2}} (\text{mol}^2 \text{kg}_{\text{solvent}}^{-2}). \quad (\text{B.10})$$

Using Eq. (B.10) in Eq. (B.9) gives

$$r = \frac{k_{\text{OH}^-}}{k^m(\gamma) \gamma_{\text{OH}^-} \gamma_{\text{CO}_2}} \frac{\rho^2 \cdot r^m}{(1 + \sum_{\text{all ions } i} m_i M_i)^2}. \quad (\text{B.11})$$

Rearranging yields

$$k^m(\gamma) = \frac{k_{\text{OH}^-}}{\gamma_{\text{OH}^-} \gamma_{\text{CO}_2}} \frac{\rho^2 (r^m / r)}{(1 + \sum_{\text{all ions } i} m_i M_i)^2}. \quad (\text{B.12})$$

Now a final link between the ratio of r (see Eq. (B.8)) and r^m (see Eq. (B.7)) will eliminate these parameters from the equation

$$\frac{r}{r^m} = \rho - \sum_{\text{all ions } i} c_i M_i \rightarrow \frac{r^m}{r} \\ = \frac{1}{\rho - \sum_{\text{all ions } i} c_i M_i} \left(\frac{\text{kg}_{\text{solvent}} * 1000}{m_{\text{solution}}^3} \right). \quad (\text{B.13})$$

Using the last two equations gives the relation to calculate $k_{\text{OH}^-}^m(\gamma)$ from k_{OH^-} :

$$k_{\text{OH}^-}^m(\gamma) = \frac{k_{\text{OH}^-}}{\gamma_{\text{OH}^-} \gamma_{\text{CO}_2}} \\ \times \frac{\rho^2}{(1 + \sum_{\text{all ions } i} m_i M_i)^2 (\rho - \sum_{\text{all ions } i} c_i M_i)}. \quad (\text{B.14})$$

Appendix C. Experimental data

C.1. Experimental data for the kinetics of CO₂ in “pure” aqueous sodium hydroxide solutions

Table C1 shows the kinetic constants derived from own measurements.

C.2. Applied activity coefficients to derive the activity-based kinetics for the reaction of CO₂ in “pure” aqueous sodium hydroxide solutions

Table C2 presents the activity coefficients of CO₂ and OH[−] for the system NaOH–CO₂–water.

Table C1
Kinetic constants derived from own measurements (as shown in Fig. 2)

c_{NaOH} (kmol m ^{−3})	k_1 (s ^{−1})	k_{OH^-} (m ³ kmol ^{−1} s ^{−1})
0.7848	10 404	13 257
0.8981	12 022	13 386
1.4852	23 862	16 067
1.9797	38 747	19 572
2.2679	48 117	21 217
2.464	55 342	22 460
2.9599	72 594	24 526
3.0076	83 849	27 879

Table C2

Activity coefficients of CO₂ and OH[−] for the system NaOH–CO₂–water

c_{NaOH}	γ_{CO_2}	γ_{OH^-}
0	1.0000	0.9857
0.1	1.0245	0.7796
0.2	1.0495	0.7382
0.3	1.0752	0.7167
0.4	1.1015	0.7037
0.5	1.1284	0.6955
0.6	1.1560	0.6903
0.7	1.1843	0.6872
0.8	1.2132	0.6856
0.9	1.2429	0.6852
1	1.2733	0.6858
1.1	1.3044	0.6871
1.2	1.3363	0.6891
1.3	1.3690	0.6916
1.4	1.4025	0.6946
1.5	1.4368	0.6981
1.6	1.4719	0.7019
1.7	1.5079	0.7061
1.8	1.5448	0.7106
1.9	1.5826	0.7154
2	1.6213	0.7204
2.1	1.6609	0.7258
2.2	1.7015	0.7313
2.3	1.7431	0.7371
2.4	1.7858	0.7432
2.5	1.8294	0.7494
2.6	1.8742	0.7559
2.7	1.9200	0.7625
2.8	1.9669	0.7694
2.9	2.0150	0.7764
3	2.0643	0.7837

Table C3

Raw data: absorption experiments of CO₂ in salt-doped NaOH solutions

c_{NaOH} (kmol m ^{−3})	Salt	c_{Salt} (kmol m ^{−3})	p_{CO_2} (mbar)	Flux (mmol m ^{−2} s ^{−1})	$D_{\text{CO}_2-\text{salt}}$ 10 ^{−9} (m ² s ^{−1})	$m_{\text{CO}_2-\text{salt}}$ (m ² s ^{−1})	k_{OH^-} (m ³ kmol ^{−1} s ^{−1})
0.940	LiCl	0.5	10.4	0.673	1.51	0.519	6769
0.965	NaCl	0.5	10.3	0.826	1.50	0.486	11 377
0.964	KCl	0.5	12.5	0.857	1.50	0.498	11 648
1.453	LiCl	0.5	12.7	0.846	1.35	0.422	11 621
1.465	NaCl	0.5	11.8	0.894	1.35	0.397	14 542
1.450	KCl	0.5	15.6	0.919	1.35	0.410	14 570
1.920	LiCl	0.5	11.3	0.891	1.23	0.350	15 612
0.910	LiCl	1.5	13.9	0.638	1.46	0.432	9297
1.937	NaCl	0.5	12.6	0.893	1.23	0.329	17 660
0.974	NaCl	1.5	14.6	0.705	1.44	0.357	15 736
1.936	KCl	0.5	11.5	0.975	1.23	0.337	20 053
0.930	KCl	1.5	11.8	0.872	1.46	0.391	20 869
1.427	LiCl	1.5	15.6	0.698	1.32	0.351	11 957
1.413	NaCl	1.5	12.3	0.813	1.32	0.299	22 503
1.394	KCl	1.5	13.9	0.939	1.33	0.325	25 780
1.903	LiCl	1.5	14.2	0.725	1.20	0.290	15 613
1.885	NaCl	1.5	15.8	0.805	1.20	0.248	26 593
1.865	KCl	1.5	12.9	0.988	1.20	0.269	34 272

C.3. Raw data: absorption experiments of CO₂ in salt-doped NaOH solutions

Table C3 presents the raw data of absorption experiments of CO₂ in salt-doped NaOH solutions.

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